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## CAPILLARY MOVEMENT OF GAS INCLUSIONS IN FIRING GLASS COATINGS

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The effect of iron oxides on the physicochemical properties of primer enamels that regulate capillary movement of gas bubbles was investigated. The rates of capillary movement of bubbles in an enamel melt were calculated based on two mechanisms: thermodynamic and Marangoni film flow. The duration of migration of gas bubbles from the enamel layer under the effect of capillary force was determined in approximating the predominant role of the thermodynamic mechanism.

The macrostructure of enamels determines their performance properties, so that it is necessary to know the mechanisms of distribution, concentration, and size of gas bubbles in the bulk. The presence of large bubbles causes rejection of enameled items, in particular, overfiring and burnout. The possibility of affecting the behavior of the bubbles allows controlling the quality of enamel coatings.

One feature of glassy coatings on metals is the inhomogeneity of the composition of the oxide-silicate film caused by exchange reactions on the metal–enamel interface, accompanied by migration of iron oxides into the enamel melt. When the primer is fired, the thin contact layer of the oxide melt becomes rich in iron oxides, and their content can reach 10–15% and more. The gas bubbles formed on the metal–primer melt interface are in the zone of a variable concentration of iron oxides.

We investigated the effect of iron oxides on the physicochemical properties of primer enamels that regulate capillary movement of gas bubbles. The surface tension gradient over the height of the enamel layer that appears in firing  $d\sigma/dh$  causes movement of the bubbles, which is prevented by the viscous resistance of the melt. Using the experimental values of the viscosity  $\eta$  and surface tension  $\sigma$  obtained, the rates of capillary movement of gas bubbles in an enamel melt were calculated. Enamels from frits GK-321, GK-326, GK-331 and composition C of these three frits used in concrete enamel production were selected as the initial melts. The studies were conducted on each initial melt with a different  $\text{Fe}_2\text{O}_3$  content: 0, 1, 2, 4, 6, 9, 12, and 15%.<sup>2</sup>

The surface tension of the enamel melts was investigated by the sessile drop method at 800–850°C. The dependence  $\sigma = \sigma(\text{Fe}_2\text{O}_3)$  of all enamels investigated has a minimum at a 8–10%  $\text{Fe}_2\text{O}_3$  content (Fig. 1). This is probably due to rearrangement of the structure of the melt, and the subsequent height of the curves is caused by crystallization. The gas bubbles in the bulk of the melt thus have an interface with the enamel when the surface tension changes.

The viscosity of the enamels was measured by the cylindrical indenter impression method. The effect of the temperature on the viscosity of the outer layer of primer at different concentrations of iron oxide is shown in Fig. 2. Similar dependences were obtained for all enamels studied. The position of the curves changes nonproportionally when the concentration of  $\text{Fe}_2\text{O}_3$  increases, probably due to crystallization.

The activation energy of viscous flow  $E_\eta$  was determined with the experimental data obtained at a temperature above the flow temperature. The activation energy of viscous flow

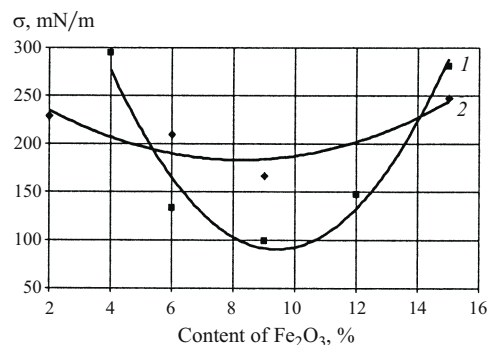
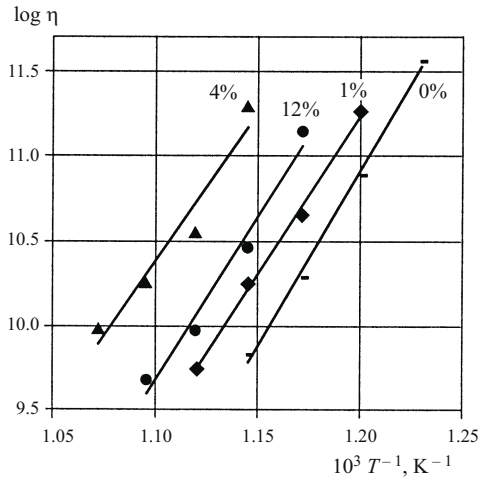


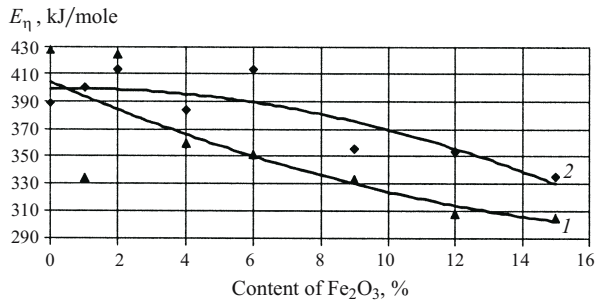
Fig. 1. Surface tension  $\sigma$  as a function of  $\text{Fe}_2\text{O}_3$  content: 1) GK-321 frit; 2) composition C.

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<sup>2</sup> Hear and below — the weight content.



**Fig. 2.** Logarithm of the viscosity  $\eta$  of the outer layer of primer on the reciprocal of the temperature.



**Fig. 3.** Activation energy of viscous flow  $E_\eta$  as a function of  $\text{Fe}_2\text{O}_3$  content: 1) GK-321 frit; 2) composition C.

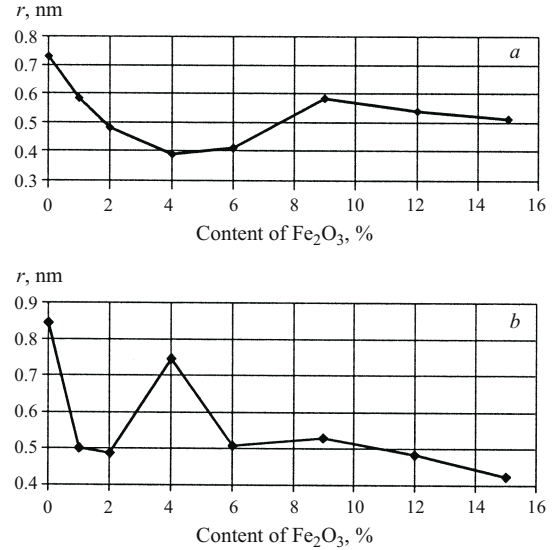
gradually decreased with an increase in the iron oxide content in the enamel, varying from 300 to 400 kJ/mole (Fig. 3).

By comparing the activation energy calculated with the hole model of a liquid with the experimental values of the activation energy (see Fig. 3), the size (nm) of the structural unit of viscous flow was estimated:

$$r = \sqrt{\frac{10^3 E_\eta}{10^{-3} \times 4\pi\sigma\text{Na}}},$$

where Na is Avogadro's constant,  $\text{Na} = 6.022 \times 10^{23} \text{ mole}^{-1}$ .

As expected, groups which are silicon – oxygen tetrahedrons, perhaps with the participation of a boron cation as the central ion, are the unit of viscous flow. Such large cations slow contiguous layers of the flowing liquid, determining its viscosity. As a consequence, the structure of the enamels is represented by a network of silicon – boron – oxygen complexes. The appearance of iron oxides slightly reduces the activation energy of viscous flow and has little effect on the size of the structural unit that determines the viscosity of the melt (Fig. 4).



**Fig. 4.** Size  $r$  of the structural unit of viscous flow as a function of  $\text{Fe}_2\text{O}_3$  content: a) GK-331 frit; b) composition C.

The rate of capillary movement of gas bubbles due to a surface tension gradient was estimated according to the thermodynamic mechanism [1, 2], taking into account passage of a bubble into a region with lower surface tension, using the equation:

$$v = \frac{2R}{3\eta} \frac{d\sigma}{dh}, \quad (1)$$

where  $R$  is the bubble radius;  $d\sigma/dh$  is the surface tension gradient over the height  $h$  of the enamel layer.

The equation was obtained by comparing the capillary force that causes the bubble to move with the force of Stokes viscous drag.

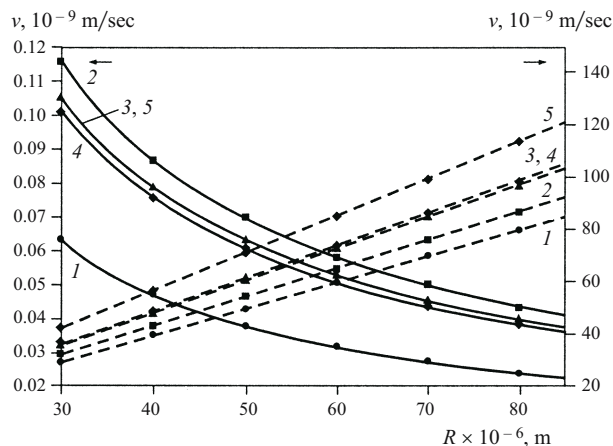
There is another approach to calculating the rate of movement based on the Marangoni effect [2]. In this case, the rate of movement of the gas bubbles is described by the equation:

$$v' = \frac{3\varepsilon^2}{4R\eta} \frac{d\sigma}{dh}, \quad (2)$$

where  $\varepsilon$  is the depth of capillary flow calculated with the equation from [3]:

$$\varepsilon = r \left( \exp \frac{\sigma\pi r^2}{3RT} - 1 \right).$$

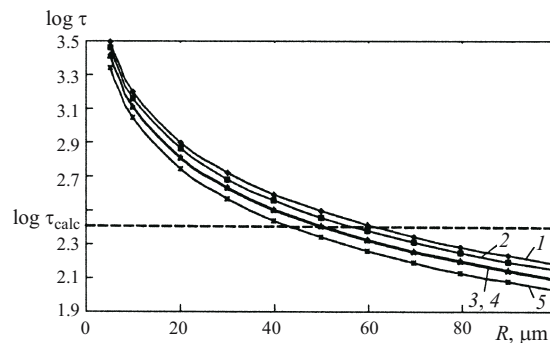
The rates of movement of gas bubbles calculated from the thermodynamic analysis — Eq. (1) — and the film flow mechanism — Eq. (2) — are shown in Fig. 5. Here and in the following calculations, the surface tension gradient was determined in the assumption of  $h = 5 \times 10^{-5} \text{ m}$  and  $\Delta\sigma = \sigma_{\text{in}} - \sigma_{\text{min}}$ . A linear dependence of the rate of movement of



**Fig. 5.** Rate of movement of gas inclusions as a function of their size: 1) outer primer; 2, 3, 4, and 5) frits GK-321, GK-326, GK-331, and C1, respectively; dashed and solid curves) calculation according to the thermodynamic mechanisms and the film flow mechanism.

gas bubbles on their size was obtained in the first case, and the dependence in the second case was inversely proportional, and consequently the smaller the bubbles, the more rapidly they move.

In approximating the predominant role of the thermodynamic mechanism, the duration of migration of gas bubbles from the enamel layer under the effect of capillary force was calculated. The calculations were performed for the viscosity corresponding to the firing temperature. Since firing takes place relatively rapidly in production of an enamel coating (3–4 min at the highest temperature), not all of the bubbles can be removed from the layer of enamel melt. Large gas inclusions ( $R > 50 \mu\text{m}$ ) leave the enamel layer and some of the small inclusions ( $R < 435 \mu\text{m}$ ) remain in the enamel film



**Fig. 6.** Effect of the size of gas inclusions on the duration of their migration from an enamel melt film: 1) outer primer; 2, 3, 4, and 5) frits GK-321, GK-326, GK-331, and C1, respectively.

(Fig. 6), forming the macrostructure of the applied enamel coat.

Small bubbles are distributed in the bulk of the film, providing the required elastic properties of the enamel coating after the melt hardens. In this case, the probability of formation of chips and cracks in the enamel layer with acceptable performance strains of the metal base.

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